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Reactions of Heterocumulenes with Organometallic Reagents: XIV.* Quantum-Chemical Study on the Mechanism of Unusual Thermally Induced Transformation of Methyl *N*-Methylbuta-2,3-dienimidothioates into Iminocyclobutenes with Migration of the Methylsulfanyl Group

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Abstract—The mechanism of formation of cyclobutene ring from methyl 2-methoxy- and 2-phenyl-*N*-methylbuta-2,3-dienimidothioates (H_2C=C=C(R)−C(SMe)=NMe, 1-aza-1,3,4-trienes) was studied by quantum-chemical methods. The limiting stage in the [1,3]-sigmatropic migration of the methylsulfanyl group was found to follow a reaction path involving a "collapsed" state of the azatriene with linear configuration of the C=N–Me fragment, which is characterized by reduced activation barrier. The results of calculations substantiate preferential formation of pyrrole and dihydropyridine heterorings in the thermolysis of methyl 2-methoxy-*N*-methylbuta-2,3-dienimidothioate and of dihydropyridine and cyclobutene structures in the thermolysis of methyl *N*-methyl-2-phenylbuta-2,3-dienimidothioate.

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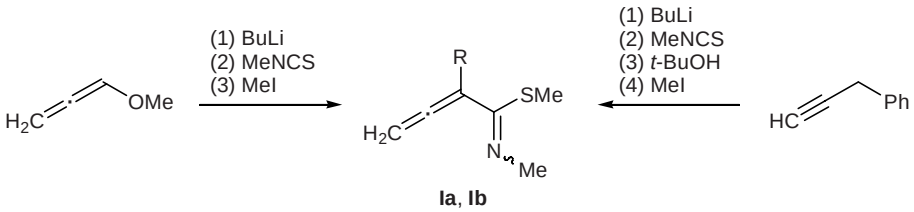
1-Aza-1,3,4-triene systems C=C=C−C=N available in almost quantitative yield via reactions of lithiated allenes or alkynes with isothiocyanates possess uniquely high reactivity in thermal cyclizations with formation of various cyclic structures (pyrrole, dihydropyrrole, dihydropyridine, pyridine, quinoline, thiophene, thietane derivatives, etc.), which makes them quite valuable synthetic intermediates and building blocks [2, 3]. We have recently discovered one more novel thermal rearrangement of 1-aza-1,3,4-trienes, in particular alkyl *N*-alkyl-2-phenylbuta-2,3-dienimidothioates into isomeric iminocyclobutenes [4]. Specific features of this rearrangement are the formation of a carbocycle instead of heteroring and change of the sequence of the NR and SR heteroatom-containing substituents as compared to the linear precursor.

Diversity of reaction channels in transformations of 1-aza-1,3,4-trienes is largely determined by their high rotational mobility and high probability for various intramolecular rearrangements which are often limiting stages in tandem cyclizations [5, 6]. Detailed study of the entire elementary step sequence in the cyclization

Scheme 1.



Ia, **Ib**

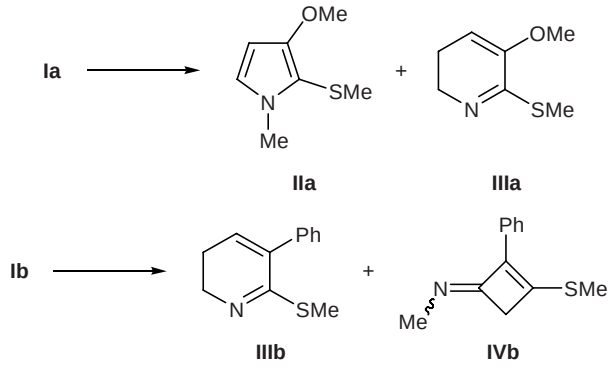
R = OMe (**a**), Ph (**b**).

* For communication XIII, see [1].

process could give rise to recommendations concerning improvement of the yield of the target product and reaction selectivity.

In the present work we analyzed the total potential energy surfaces (PES) for the thermally induced cyclizations of 1-aza-1,3,4-triene systems into cyclobutene structures. As substrates we selected methyl 2-methoxy-*N*-methylbuta-2,3-dienimidothioate (**Ia**) and methyl *N*-methyl-2-phenylbuta-2,3-dienimidothioate (**Ib**) (Scheme 1) whose transformations could lead (with higher or lower probability) to pyrrole, dihydropyridine [5, 6], or cyclobutene structures (Scheme 2).

Scheme 2.



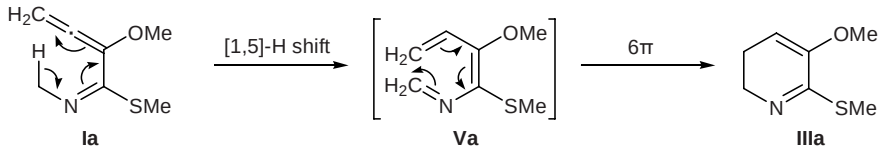
As shown previously [7], thermolysis of compound **Ia** gives a mixture of five- and six-membered nitrogen-containing heterocycles, pyrrole **IIa** and 2,3-dihydropyridine **IIIa** at a ratio of ~2:1. However, replacement of the methoxy group in azatriene **Ia** by phenyl unexpectedly led to qualitatively different results of the cyclization. Heating of azatriene **Ib** for 0.5 h at 120°C, apart from the expected six-membered heterocycle, 2,3-dihydropyridine **IIIb** (yield 55%), gave four-membered cyclobutene derivative **IVb** (yield 28%) [4]. It should be emphasized that we detected neither cyclobutene structure among the thermolysis products of azatriene **Ia** nor pyrrole structure among the thermolysis products of azatriene **Ib**. The observed difference in the products structure upon variation of substituent at the α-allenic carbon atom in **I** could not be expected *a priori*, and it is difficult to rationalize without considering the cyclization mechanisms.

All calculations were preformed with the aid of Gaussian 98 software package [8] using 6-31G* basis set. The molecular structures and the corresponding gradient channels were calculated in terms of the density functional theory (DFT) using three-parameter B3LYP functional [9]. The geometric parameters of molecular systems were optimized up to a value of 10^{-5} a.u./bohr. In the analysis of flat PES areas, the gradient was set at a level of 10^{-6} a.u./bohr. Stationary points were localized by analysis of the Hesse matrix. Transition states were identified by the linear synchronous transit-guided quasi-Newton method (QST2) [10]. Approximate transition state structure thus determined was then refined using the quadratic synchronous transit protocol (QST3) [10]. Analysis of vibration frequencies at saddle points was performed, and conformity of critical points to the gradient line connecting them was proved by the internal reaction coordinate (IRC) technique. The energies of zero-point harmonic vibrations (*ZPE*) were calculated with the use of a calibration factor of 0.9806 [10].

We previously [5] reported on B3LYP/6-31G** calculations of the gradient channel of formation of dihydropyridine **IIIa** by thermolysis of azatriene **Ia**. It was found that the reaction includes two consecutive stages: [1,5]-H shift and 6π-electrocyclization of conjugated 2-aza-1,3,5-triene **Va** [Scheme 3, reaction (1)]. Although intermediate **Va** was not detected among products of thermally induced rearrangements of 1-aza-1,3,4-triene **Ia** (because of its thermodynamic instability), the calculated data were reliably proved by numerous experiments involving isomerizations of 1-aza-1,3,4-trienes into 2-aza-1,3,5-trienes (the latter were isolated and characterized) [2]. The energies of activation of the elementary stages were estimated at 114.3 and 90.1 kJ/mol, respectively.

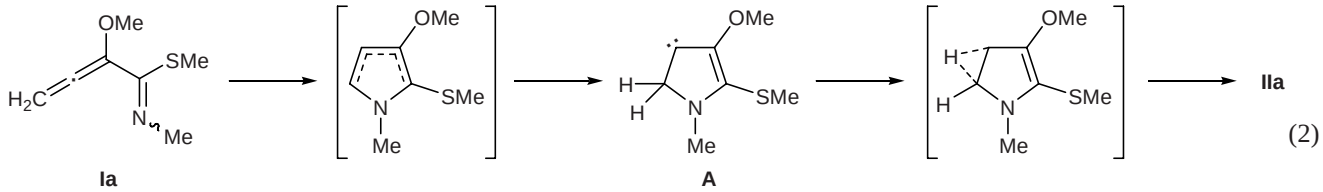
Possible mechanisms of cyclization of azatriene **Ia** to pyrrole structure **IIa** were considered in [5, 6]. Analysis of the potential energy surface revealed two most probable channels for the formation of pyrrole ring. The first of these involves cyclization of protonated structure **Ia**. According to the B3LYP/6-31G** calculations, its activation barrier is 44.9 kJ/mol [5]. Following the second path, pyrrole ring is formed via

Scheme 3.



(1)

Scheme 4.



(2)

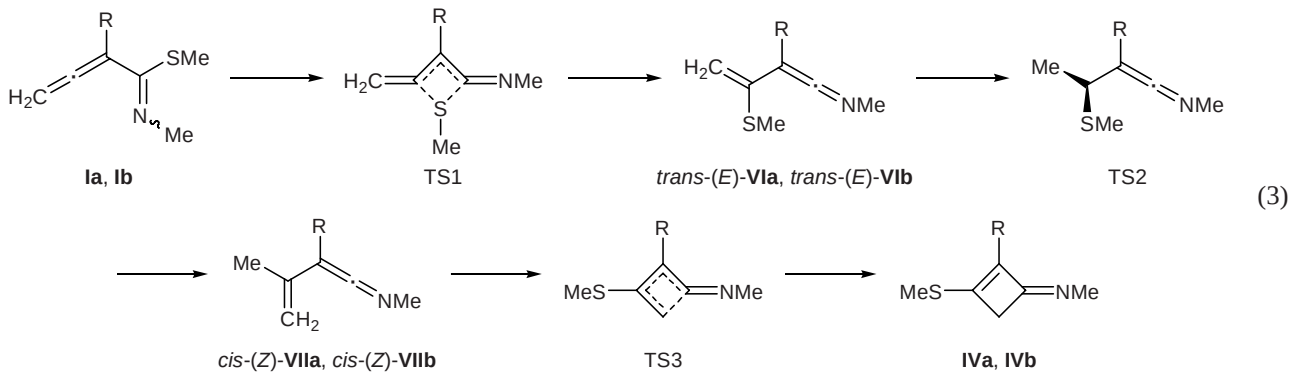
direct nucleophilic attack by the nitrogen atom on the terminal carbon atom in the allene fragment through cyclic carbene **A** as key intermediate [Scheme 4, reaction (2)] [6]. Here, the rate-determining stage (B3LYP/6-311G** calculations) is ring closure with formation of carbenoid structure **A** (E_a = 96.2 kJ/mol). [4,5]-Hydride shift in **A** is characterized by an activation barrier of 61.5 kJ/mol.

A probable channel for formation of cyclobutene structure **IVb** from azatriene **Ib**, which was proposed in [4], includes [1,3]-migration of the methylsulfanyl group, followed by intramolecular [2+2]-cyclization of buta-1,3-dien-1-imine [*trans*-(*E*)-**VIb** → *cis*-(*Z*)-**VIIb** → **IVb**)]. Like 2-aza-1,3,5-triene **Vb**, structure *cis*-(*Z*)-**VIIb** was not detected experimentally. The potential energy surfaces for the formation of cyclobutene derivatives from compounds **Ia** and **Ib** were analyzed in keeping with the elementary stages shown in Scheme 5 [reaction (3)].

Rotational lability of molecule **Ia** gives rise to several stationary states whose relative stabilities were considered in [6]. On the basis of these data, we selected rotamers of **Ia** that are most sterically favorable for [1,3]-sigmatropic shift of the SMe group, specifically structures with *trans*-(*E*)-oriented allene and C=NMe fragments. According to the calculations, *syn*-(*Z*)/*anti*-(*E*) isomerism related to the presence of a C=NMe group in the molecule almost does not affect the activation parameters of the first reaction stage, isomerization of buta-2,3-dien-1-imine **Ia** into buta-1,3-dien-1-imine **VIa**. As will be shown below, a more significant factor for the [1,3]-sigmatropic rearrangement of **Ia** is a "collapsed" state which could significantly reduce the barrier to [1,3]-SMe shift. This state appears along inversion or torsion *syn*-(*Z*)/*anti*-(*E*)-isomerization path of azatriene **Ia** and is characterized by linear configuration of the C=N−Me group (Scheme 6). The total energy of compound **Ia** in the collapsed state increases by ~70–80 kJ/mol (B3LYP/6-311+G**), depending on the rotational state [1]. This is the result of rehybridization of the nitrogen atom and considerable structural reorganization of molecule **Ia**. The molecular skeleton flattens, the C=N and N−Me bonds become stronger, and the ordinary S−C and C−C bonds weaken, thus facilitating migration of the SMe group.

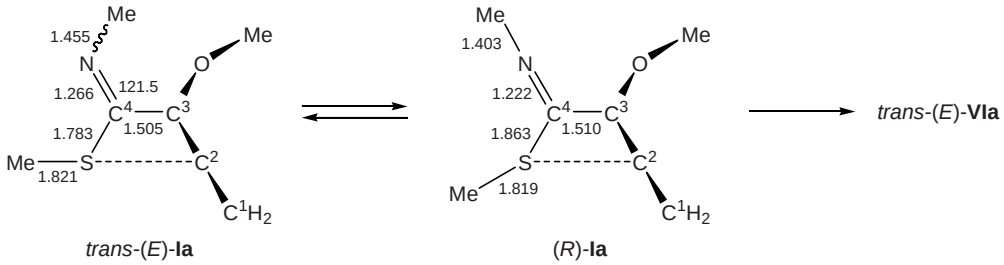
Therefore, apart from the usual channel for formation of cyclobutene structures [(*E*)-**Ia** → **VIa** → **VIIa** → **IVa**], we examined an alternative gradient channel passing through the critical point corresponding to the collapsed state [(*E*)-**Ia** → (*R*)-**Ia** → **VIa** → **VIIa** → **IVa**]. The activation parameters of the rate-determining stages in reactions (1) [5], (2) [6], and (3) were calculated with the use of different basis sets: 6-31G**, 6-311G**, and 6-31G*. With a view to obtain uniform data which could be compared with each other, we calculated the thermodynamic and kinetic parameters of the first two reactions using 6-31G* basis set. The relative difference in the obtained values, depending on the basis set used, was 0–2 kJ × mol^{-1} for the activation parameters and 1–4 kJ/mol for

Scheme 5.



(3)

Scheme 6.



the thermodynamic parameters. Taking into account the corresponding absolute values, comparison of the obtained data with those reported in [5, 6] seems to be appropriate.

Analysis of the potential energy surface for the transformation **Ia** → **IVa** showed that the first stage involving [1,3]-sigmatropic rearrangement is rate-determining (Fig. 1, Table 1). Its activation barrier along the gradient channel involving no collapsed state is 148.4 kJ/mol. Structure **VIa** is slightly less stable that the initial state (by 4.7 kJ/mol). The barrier to the rotation *trans–cis* isomerization **VIa** → **VIIa** is not high (21.0 kJ/mol).

Structure *cis*-(*Z*)-**VIIa** is less stable than *trans*-(*E*)-**VIa** by 5.6 kJ/mol. Closure of isomer **VIIa** with formation of cyclobutene fragment is characterized by an activation energy of 78.7 kJ/mol. On the whole, the reaction is exothermic. The total heat balance of the rearrangement (*E*)-**Ia** → **IVa** was estimated at 40.6 kJ/mol. The reaction channel involving structures (*R*)-**Ia** and (*R*)-**VIa** was examined as follows. Structural parameters of (*R*)-**Ia** and (*R*)-**VIa** (Fig. 2) were determined in the "fixed scan" mode with linear configuration of the C=N−Me fragment and full optimization of the other geometric parameters, and the corresponding transition state (*R*)-TS1 was then localized. Collapsed structures (*R*)-**Ia** and (*R*)-**VIa** are less stable than (*E*)-**Ia** and **VIa**: ΔE = 72.6 and 41.1 kJ/mol, respectively; the gradient channel involving these structures is characterized by reduced activation barrier in the limiting stage (by 13.9 kJ/mol).

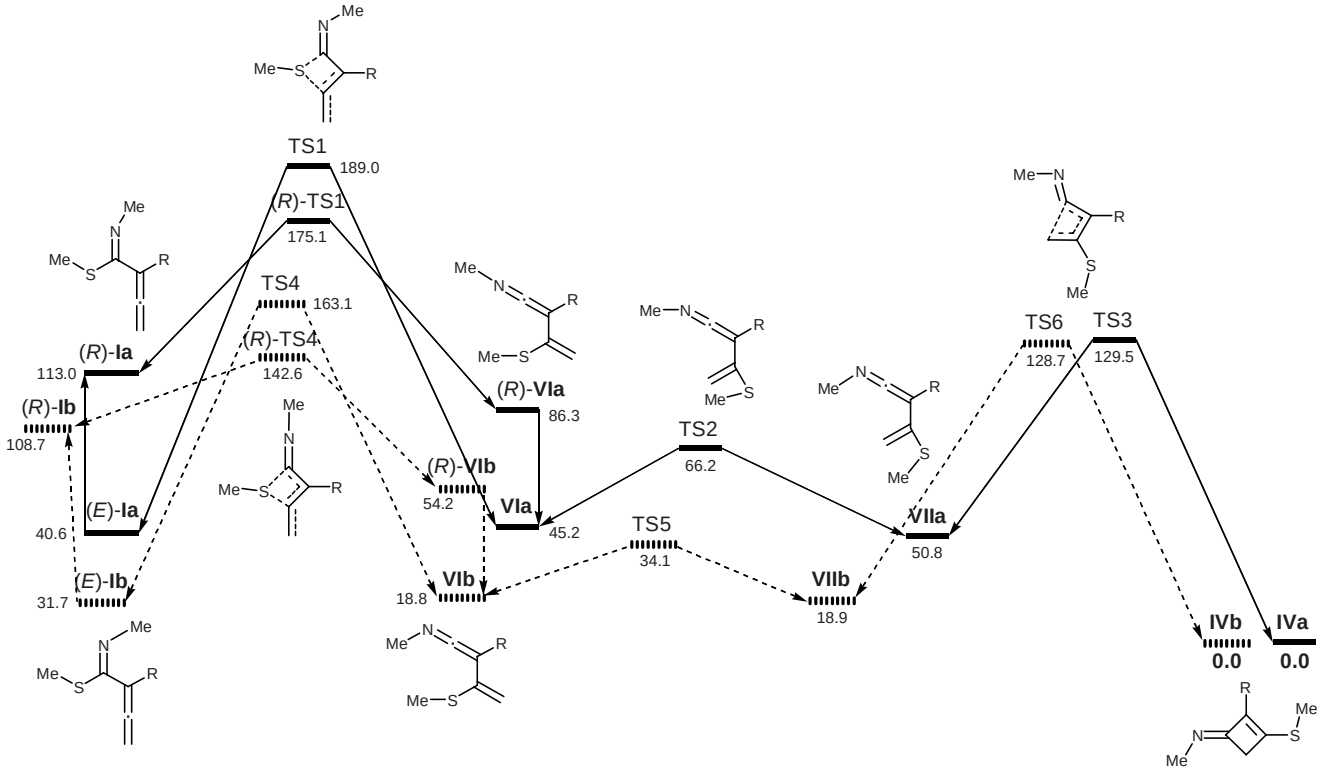


Fig. 1. Mechanism of formation of cyclobutene ring and evolution of the molecular structure of compound **Ia** (solid lines) and **Ib** (dashed lines) according to the B3LYP/6-31G* calculations.

Participation of the (*R*)-structures in the [1,5]-H shift (Scheme 3) or direct nucleophilic attack by the nitrogen atom on the terminal allene carbon atom (Scheme 4) increases the activation barriers due to enhanced double-bond character of the C=N−Me fragment. Analysis of the obtained data showed that the formation of cyclobutene ring from azatriene **Ia**, even with participation of the (*R*)-states, requires appreciably higher activation energy (134.5 kJ/mol), as compared to the formation of pyrrole (96.2 kJ/mol) and dihydropyridine structures (114.3 kJ/mol). This is consistent with the experimental data and explains the absence of cyclobutene derivative among the thermolysis products of azatriene **Ia**.

Replacement of the methoxy group in **Ia** by an aromatic ring considerably restricts rotational freedom of molecule **Ib**, which differently affects the kinetic parameters of the gradient channels for the rate-determining stages of reactions (1)–(3). In the optimal conformation, the allene fragment and benzene ring lie in one plane, and the imidothioate moiety is almost orthogonal to that plane. Free rotation about the C−Ph bond is restricted due to conjugation and spatial interaction with one of the methyl groups. The low-energy ($\Delta E \leq 30$ kJ/mol) variations of the dihedral angle $C^2C^3C^4N$ in the imidothioate group are limited to ±25°. Rotational isomerism of **Ib** is thus reduced to *syn*-(*Z*)/*anti*-(*E*) isomerism with respect to the C=N bond and torsion rotation of the SMe group.

The change in the activation energy in going from azatriene **Ia** to compound **Ib** is minimal in reaction (1). The barrier to the [1,5]-H shift decreases by 5.5 kJ/mol (Fig. 3, Table 2), and deviation of the allene fragment from the benzene ring plane in transition state TS7 does not exceed 17°. The activation parameter changes more appreciably in reaction (2) at the stage involving direct nucleophilic attack. The reason is considerable structural reorganization of the molecular skeleton, which includes transition from orthogonal arrangement of the imidothioate and allene fragments to almost planar in TS8. As a result, the activation barrier increases to 137.3 kJ/mol against 96.2 kJ/mol for azatriene **Ia**. Intermediates **B** and **C** are thermodynamically less stable than initial rotamer (*E*)-**Ib**: ΔE = 11.1 and 114.1 kJ/mol, respectively (Table 2).

In going from structure **Ia** to **Ib**, the first two stages of reaction (3), [1,3]-sigmatropic rearrangement **Ib** → **VIb** and *trans*/*cis*-rotational transition **VIb** → **VIIb**, change their profiles (Fig. 1). Their activation barriers decrease by 25.9 and 32.1 kJ/mol, respectively. The third stage (cyclobutene ring closure) almost does not depend on the R substituent (Fig. 1, Table 1). The total heat balance of exothermic reaction (3) with compound **Ib** is 31.7 kJ/mol.

Table 1. Total energies (E_{tot}, a.u.), energies of zero-point harmonic vibrations (*ZPE*, a.u.), relative energies (ΔE, kJ/mol), imaginary or least harmonic frequencies (iw/w_1, cm^{-1}), and electrical dipole moments (μ, D) for stationary, transition, and collapsed states in reaction (3), calculated by the B3LYP/6-31G* method

Structure	$-E_{tot}$	*ZPE*	ΔE	iw/w_1	μ
(*E*)-**Ia**	801.43546	0.16868	40.6	33	2.00
TS1	801.37619	0.16626	189.8	*i*413	0.87
(*E*)-**VIa**	801.43546	0.16893	45.2	45	0.86
TS2	801.42592	0.16859	66.2	*i*428	1.03
(*Z*)-**VIIa**	801.43179	0.16893	50.8	41	3.14
TS3	801.40052	0.16762	129.5	*i*481	3.39
IVa	801.45337	0.17117	0.0	45	2.79
(*R*)-**Ia**	801.40617	0.16696	113.0	*i*296	1.55
(*R*)-TS1	801.38191	0.16637	175.1	*i*433	2.50
(*R*)-**VIa**	801.41702	0.16767	86.3	*i*294	2.93
(*E*)-**Ib**	917.97446	0.21585	31.7	67	1.11
TS4	917.92012	0.21152	163.1	*i*553	1.97
(*E*)-**VIb**	917.97774	0.21417	18.8	83	1.86
TS5	917.97162	0.21388	34.1	*i*367	0.99
(*Z*)-**VIIb**	917.97760	0.21407	18.9	78	1.27
TS6	917.93562	0.21396	128.7	*i*590	3.74
IVb	917.98852	0.21787	0.0	98	1.98
(*R*)-**Ib**	917.94279	0.21344	108.7	*i*382	1.73
(*R*)-TS2	917.92822	0.21182	142.6	*i*507	3.60
(*R*)-**VIb**	917.96427	0.21420	54.2	*i*378	3.84

The direct [1,3]-sigmatropic rearrangement in molecule **Ib** [without participation of the (*R*)-state of the

Table 2. Total energies (E_{tot}, a.u.), energies of zero-point harmonic vibrations (*ZPE*, a.u.), relative energies (ΔE, kJ/mol), imaginary or least harmonic frequencies (iw/w_1, cm^{-1}), and electrical dipole moments (μ, D) for structures formed in the rate-determining stages of reactions (1) and (2), calculated by the B3LYP/6-31G* method

Structure	$-E_{tot}$	*ZPE*	ΔE	iw/w_1	μ
(*E*)-**Ib**	917.97446	0.21585	0.0	67	1.11
TS7	917.93117	0.21377	108.8	*i*786	2.87
B	917.97067	0.21631	11.1	48	1.15
TS8	917.91778	0.21142	137.3	*i*459	3.87
C	917.93407	0.21900	114.1	51	6.31

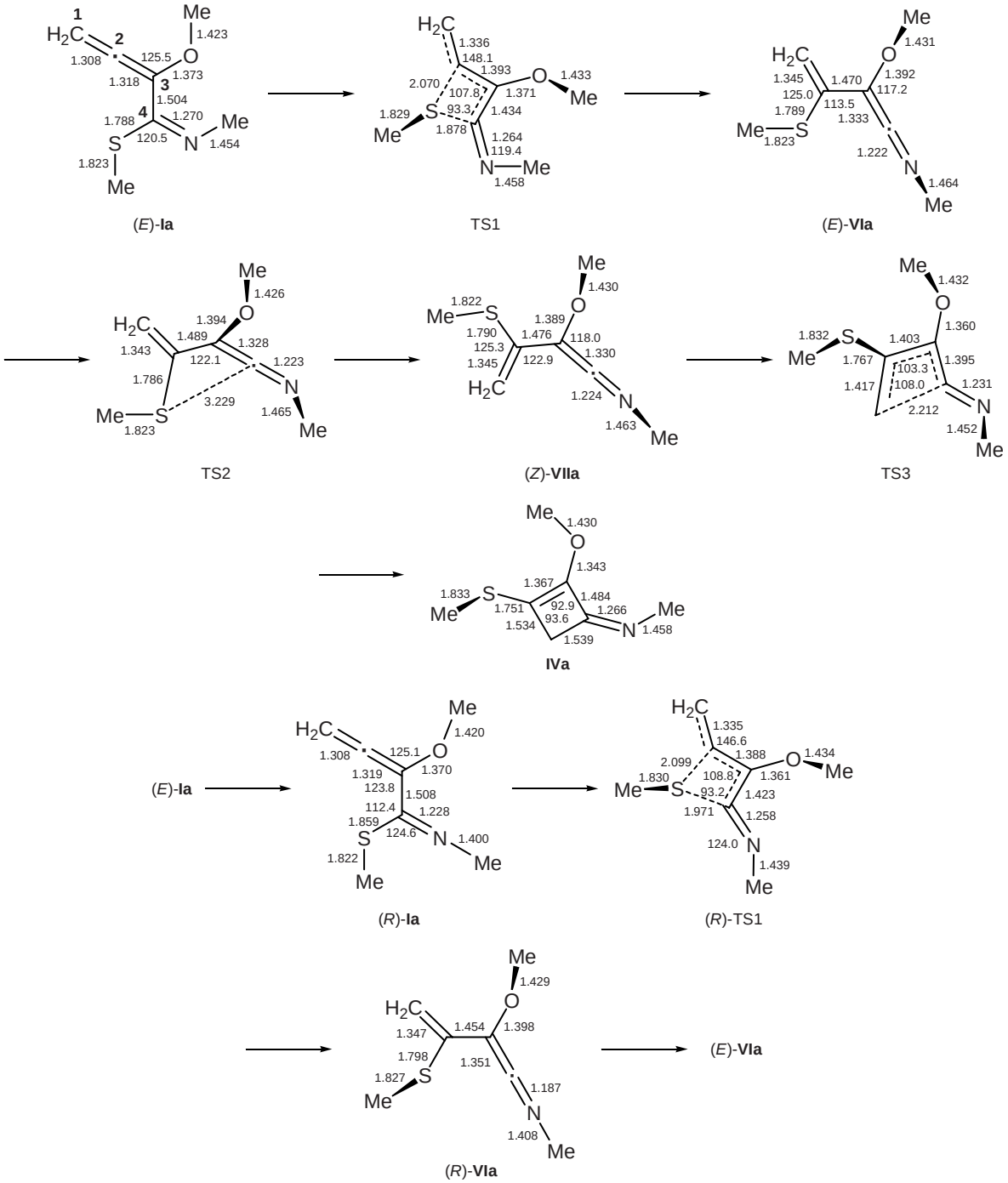


Fig. 2. Structures and principal geometric parameters of stationary, metastable, and transition states along the reaction channels (*E*)-**Ia** → **IVa** and (*R*)-**Ia** → **IVa**, according to the B3LYP/6-31G* calculations (here and in Figs. 3–5, the bond lengths are given in Å, and the bond angles, in deg).

C=NMe group] is characterized by an activation barrier of 131.4 kJ/mol, which is comparable to the barrier in the limiting stage for the formation of pyrrole ring (137.3 kJ/mol). If the gradient channel involves structure (*R*) (the procedure is described above for azatriene **Ia**), the activation barrier decreases by 20.5 kJ/mol due to considerable weakening of the C−S bond in the collapsed state (Fig. 4); as a result, channel (3) becomes more probable than (2) and comparable to channel (1). As with compound **Ia**, the collapsed state (*R*) does not stabilize transition state structures in reactions (1) and (2). The calculated kinetic parameters of reactions (1)–

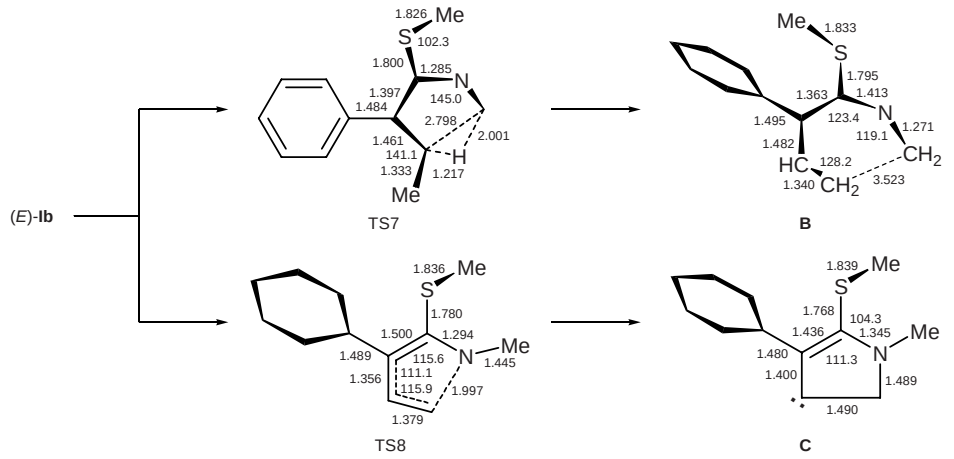


Fig. 3. Structures and principal geometric parameters of stationary and transition states along the reaction channels (*E*)-**Ib** → **B** and (*E*)-**Ib** → **C**, according to the B3LYP/6-31G* calculations.

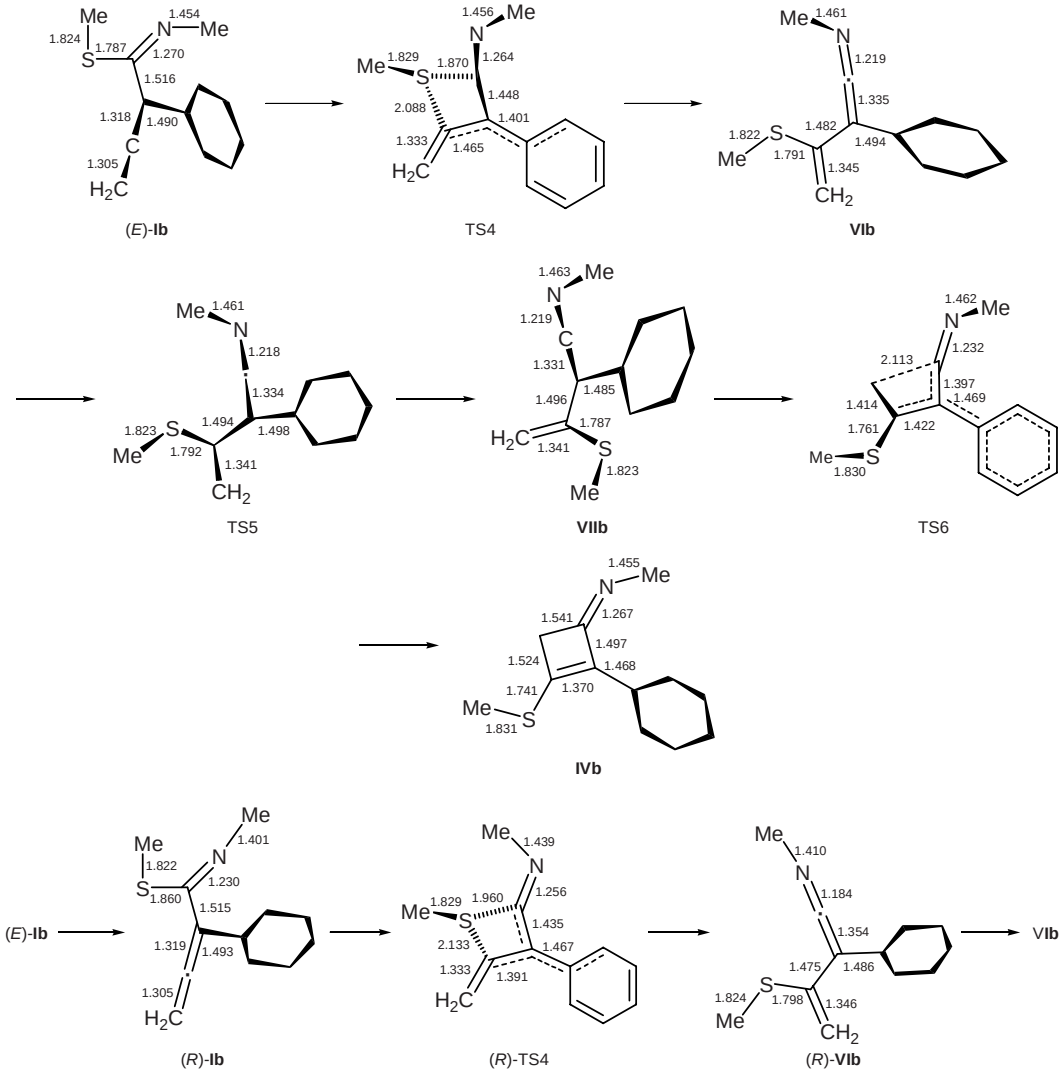
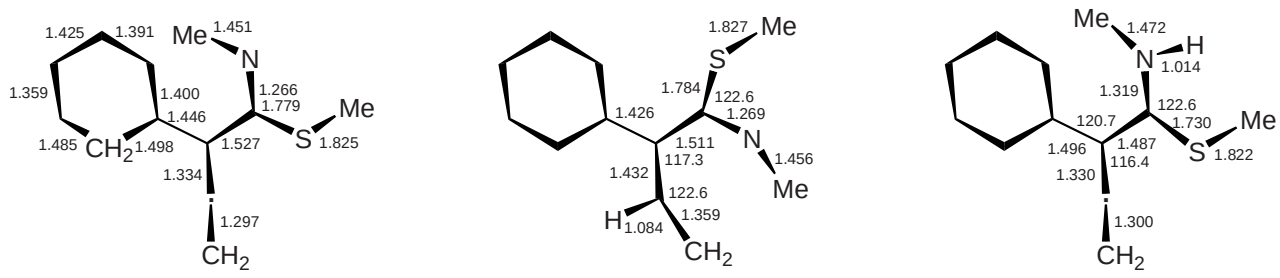


Fig. 4. Structures and principal geometric parameters of stationary, metastable, and transition states along the reaction channels (*E*)-**Ib** → **IVb** and (*R*)-**Ib** → **IVb**, according to the B3LYP/6-31G* calculations.



Ib (PhH^+) **Ib** ($C^\beta H^+$) **Ib** (NH^+)

E_{tot}, a.u.	–918.30400	–918.34627	–918.34473
ZPE, a.u.	0.22700	0.22967	0.23082

Fig. 5. Structures and principal geometric parameters of protonated forms of compound (*E*)-**Ib**, according to the B3LYP/6-31G* calculations.

(3) explain well absolute prevalence of dihydropyridine **IIIb** and cyclobutene **IVb** among the thermolysis products of compound **Ib**.

In order to obtain a complete pattern of the cyclization of compound **Ib**, it is necessary to analyze another hypothetically possible channel for the formation of pyrrole structure **IIb**, which involves protonated azatriene **Ib**. Protonation of **Ib** is likely to be significant in protic medium. Here, as with azatriene **Ia** [5], the most favorable for cyclization is attack by proton at the C_β atom on the π orbital localized on the C_β and C_γ atoms of the allene fragment. As a result, *p* orbital on the C_γ atom is activated to interaction with the nitrogen π orbital. However, azatriene **Ib** possesses two more protonation centers, the nitrogen atom and benzene ring. With a view to estimate the probabilities for formation of alternative protonated structures **Ib**($C_\beta H^+$), **Ib**(PhH^+), and **Ib**(NH^+), we calculated their relative stabilities and proton affinities (*PA*). The proton affinities were calculated by the standard formula: *PA*(B) = $\Delta E_{tot} - \Delta ZPE$, where $\Delta E_{tot} = E(B) - E(BH^+)$ and $\Delta ZPE = \Delta ZPE(B) - \Delta ZPE(BH^+)$]. According to [1], the most probable protonated form of compound **Ia** is **Ia**(NH^+); it is more stable than **Ia**($C_\beta H^+$) by 26.9 kJ × mol^{-1}, and its proton affinity is higher by 10.6 kcal/mol (B3LYP/6-311+G**). The calculations showed that structures formed by protonation of molecule **Ib** at different positions of the aromatic ring are considerably less stable (by more than 100 kJ/mol) than **Ib**($C_\beta H^+$), while the latter is less stable than **Ib**(NH^+) (ΔE = 45.5 kJ/mol). The geometric parameters of protonated structures **Ib**(PhH^+), **Ib**($C_\beta H^+$), and **Ib**(NH^+) are given in Fig. 5. Their relative stabilities are 149.5, 45.5, and 0.0 kJ/mol, respectively. The total energies and *ZPE* are also given in Fig. 5. The calculated proton affinities of **Ib**(PhH^+), **Ib**($C_\beta H^+$), and **Ib**(NH^+) are 199.9, 224.8, and 235.7 kcal/mol, respectively. Thus the presence in molecule **Ib** of an alternative center which is considerably more favorable for protonation (nitrogen atom) is likely to block up the pyrrole cyclization channel.

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